GLASS SUBSTRATE FOR A MASK BLANK, METHOD OF PRODUCING A GLASS SUBSTRATE FOR A MASK BLANK, MASK BLANK, METHOD OF PRODUCING A MASK BLANK, TRANSFER MASK, AND METHOD OF PRODUCING A TRANSFER MASK

The present application claims priority to prior Japanese Patent Application No. 2002-208049, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to a glass substrate for a mask blank used for a transfer mask (and a mask blank which is an original plate of the transfer mask) employed to produce semiconductor integrated circuits, liquid crystal display panels or the like, to a method of producing the glass substrate, and to a method of producing a mask blank and a transfer mask using the substrate.

A photomask blank using a glass substrate for an electronic device or an information recording medium is produced by forming a single or a plurality of layers of a functional thin film, such as a light shielding film (opaque film) that imparts optical changes in response to transfer exposure light or a phase shift film or the like, or a recording film or the like for recording information, on a glass substrate for electronic devices. In the production process of the photomask blank, the information recording medium, or other electronic devices, a defect inspection for checking for cracks existing in glass substrates is usually performed, or a defect inspection is usually performed after producing electronic devices. Defects on the glass substrates for electronic devices include scratches, stains, bubbles, striae, etc. These defects are detected by visual inspections or by using a defect inspection apparatus adapted to apply

inspection light to a surface of a glass substrate to make use of the transmitted light or scattered light from the glass substrate, thereby detecting defects.

Meanwhile, the defect inspection after an electronic device is fabricated is for checking for foreign matters or pinholes in or on a functional thin film, or checking optical characteristics, recording characteristics, etc. for any problems.

In particular, defects of cracked states referred to as "cracks" among the defects existing in glass substrates for electronic devices are formed during a grinding process or a polishing step preceding a finish polishing step that uses abrasive particles having a relatively large diameter (e.g., a polishing step using a cerium oxide as the primary ingredient). The cracks cannot be detected at all in a certain direction or are difficult to detect, because they hardly have width on the surface of a glass substrate in a certain direction.

For the defect inspections described above, the visual inspections are carried out because they advantageously permit instant inspection of a glass substrate from any directions, achieving higher efficiency and reliability, and also permit discrimination of the types of defects. However, defects of sizes that cannot be detected by human eyes, and cracks on the surface of a glass substrate are extremely small, so that they are frequently overlooked. Thus, a glass substrate that has passed a defect inspection despite of a small crack on the surface of a glass substrate is subjected to the step of forming functional thin films on the glass substrate to produce an electronic device, and the defect is detected by a defect inspection machine for the first time in the defect inspection process carried out after the electronic device is fabricated.

The crack underlies the films, making it impossible to correct it after the electronic device is fabricated. Hence, if a crack underlying films is defected after an electronic device is produced, the electronic device has to be discarded or reworked by precision-polishing the surface of the glass substrate again after removing the functional thin films. This has been posing a problem of a poor

production yield and high production cost.

The following will provide an explanation by taking a glass substrate for a photomask blank as an example of the glass substrate for an electronic device.

At present, photolithography techniques are applied in the process for forming wiring or other regions in the production of semiconductor integrated circuits or liquid crystal display panels.

In the photolithography process, the photomask used as an exposure original plate has a patterned light shielding film formed on a transparent substrate. The light shielding film pattern is transferred onto a transfer material, such as a silicon wafer or a glass substrate, through an exposure apparatus to make a semiconductor integrated circuit or a liquid crystal display panel. The characteristics of the pattern to be transferred onto the silicon wafer or the glass substrate are directly related to the light shielding film pattern formed on the photomask. It is important that the light shielding film pattern is free of any pattern defects.

The pattern defects are considered to be caused by defects underlying a film due to the defects (scratches, the adhesion of foreign matters, etc.) on the surface of the glass substrate for an electronic device, or in-film or on-film defects caused by a defect of a photomask blank (the adhesion of foreign matters or half pinholes (the pinholes formed when foreign matters on a film fall off) or the like). With the increasing miniaturization of patterns, correcting defects of fabricated electronic devices is becoming more difficult, and the criteria for surface defects in electronic device glass substrates that cannot be corrected and the accuracy of substrate configurations are becoming more strict.

As disclosed in, for example, Japanese Unexamined Patent Application Publication No. 1-40267, the glass substrates for electronic devices are produced according to a polishing method in which they are polished with an abrasive material primarily composed of cerium oxide, then subjected to finish-

polishing (precision polishing) with colloidal silica.

Fig. 6 is a diagram showing a conventional method of producing the glass substrates for electronic devices.

In Fig. 6, a rough polishing step (S601) in which the main surface of a glass substrate is polished with relatively large abrasive particles having an average particle size of about 1 μm to about 3 μm is carried out, then a precision polishing step (S602) for polishing it with relatively small abrasive particles having an average particle size of about 1 μm or less is carried out, and thereafter, a defect inspection step (S603) by visual check or the like is carried out, thus producing glass substrates.

Among the defects of glass substrates, cracks are frequently not detected until films are formed on glass substrates to make photomask blanks and subjected to inspections performed using a defect inspection apparatus, which applies inspection beams from the front/back surfaces of the photomask blanks. If photomask blanks having such under-film defects are used to make photomasks, the patterns formed on the photomasks will incur disconnection, leading to defects.

With the recent miniaturization of patterns, there has been demand for smaller line widths of the patterns drawn on photomasks and for complicated patterns. Due to such miniaturized patterns in recent years, there have been some cases where it takes a few days to make a single photomask from a single photomask blank. Hence, there should be not much trouble if defects are correctable, while it is required to remake a photomask blank from the beginning if defects are uncorrectable. There has been another problem in that even correctable defects require cost and time.

As a solution to the above problems, in order to securely remove the cracks by finish polishing, an attempt has been made to prolong the polishing time for finish polishing to secure a sufficient amount to be polished off so as to

remove the cracks.

According to this method, however, there have been quite a few cases where cracks remain due to insufficient polishing-off amount due to varied depths of cracks developed in the polishing step preceding precision polishing, although it is true that the method has contributed to the reduction in cracks.

There has been another problem in that, if the polishing time of the precision polishing is extended so as to securely remove cracks existing near a surface of a substrate, then an edge surface of the glass substrate will undesirably incur a turned-down edge.

In recent years, with the trend toward further miniaturized patterns, higher accuracy has been required for loading a photomask (reticle) on a stepper of an exposure machine, and it has been also required that glass substrates have accuracy in the configuration (flatness) of the edge surfaces of glass substrates. If the edge surfaces of glass substrates have poor configuration accuracy (e.g., turned-down edges on the substrate edge surfaces), then the suction of the substrates are not securely carried out when loading them on the steppers, resulting in poor positional accuracy at loading.

A method for screening glass substrates has been proposed in Japanese Unexamined Patent Application Publication No. 2002-201042. This method is characterized in that silica glass substrates obtained by polishing, cleaning, drying and etching sliced silica glass substrate materials are inspected to select silica glass substrates whose surfaces have no defects of 0.3 μm or more in a direction parallel to the surfaces of the substrates.

The problematic cracks (latent flaws) responsible for concave defects of glass substrates take place mostly in a grinding step (lapping step). The polishing step (rough polishing and precision polishing) following the grinding step is aimed at removing the cracks or other defects, such as scratches.

In this method, the surfaces of glass substrates are etched after lapping, rough polishing and final precision polishing, thus giving no considerations to the roughening of the glass substrate surfaces caused by etching. Furthermore, when this method is used, because of the properties of silica glass, the cracks developed in a lapping step tend to extend in the depth direction due to local pressure applied to the cracks by an abrasive composed of cerium oxide or the like during rough polishing. Thus, the cracks cannot be removed unless excessive final precision polishing (obtaining more polishing-off amount means longer polishing time) is carried out. This presents a problem of lower productivity and larger turned-down edges on the edge surfaces of glass substrates.

In addition, the amount of removal by chemical etching after the final precision polishing is 0.2 to 0.5 μm, so that the surfaces of silica glass substrates are roughened even if there are no concave defects.

The glass substrates used for lithography of mask blank glass substrates are required to exhibit higher flatness and smoothness as exposure wavelengths become shorter (with increased miniaturization of patterns). For the exposure wavelengths of an ArF excimer laser (wavelength: 193 nm) and an F2 excimer laser (wavelength: 157 nm), the smoothness is required to be 0.2 nm or less in terms of the root mean square roughness (RMS), or 0.15 nm or less in terms of the root mean square roughness (RMS) at EUV (wavelengths of 13 to 14 nm). Under the etching conditions set forth above, the surfaces of the glass substrates are roughened, failing to meet the requirements.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to solve the problems with the prior art described above, and a first object thereof is to provide a glass substrate for a mask blank with high smoothness that can be used for short wavelength ranges of the ArF excimer laser, the F2 excimer laser, the EUV, etc.,

and a method of producing the same.

A second object of the invention is to provide a glass substrate for a mask blank that has no surface defects on a main surface of the glass substrate, and a glass substrate for a mask blank that is free of influences of a turned-down edge on an edge surface of the glass substrate, and a method of producing the same.

A third object of the invention is to provide a mask blank that is free of under-film defects and can be securely loaded on a stepper of an exposure machine, and a method of producing the same.

A fourth object of the invention is to provide a transfer mask that is free of pattern defects (pattern disconnection or the like) and can be securely loaded on a stepper of an exposure machine, and a method of producing the same.

To the ends described above, the present invention provides the following constructions.

(Construction 1)

A glass substrate for a mask blank obtained by etching followed by post-processing steps, including a precision polishing step, wherein the surface roughness of a main surface of the glass substrate is 0.2 nm or less in terms of root mean square roughness (RMS).

(Construction 2)

The glass substrate for a mask blank described in Construction 1, wherein the etching has an operation for eliciting a defect remaining on the main surface of the glass substrate.

(Construction 3)

The glass substrate for a mask blank described in Construction 1 or 2, wherein a surface defect of the main surface of the glass substrate cannot be detected by visual inspection.

(Construction 4)

The glass substrate for a mask blank described in any one of Constructions 1 to 3, wherein the turned-down edge amount of a peripheral portion of the main surface of the glass substrate is from -2 μm to 0 μm.

(Construction 5)

A mask blank having a thin film that causes an optical change in response to transfer exposure light, the thin film being formed on the main surface of the glass substrate for a mask blank described in any one of Constructions 1 to 4.

(Construction 6)

A transfer mask having a thin film pattern that causes an optical change in response to transfer exposure light, the thin film pattern being formed on the main surface of the glass substrate for a mask blank described in any one of Constructions 1 to 4.

(Construction 7)

A method of producing a glass substrate for a mask blank, having a step for eliciting a defect remaining on the main surface of the glass substrate, wherein a post-processing step that includes precision polishing is carried out after the step for eliciting a defect.

(Construction 8)

The method of producing a glass substrate for a mask blank described in Construction 7, wherein the post-processing step has a precision polishing step for providing the main surface with precision polishing and a cleaning step for cleaning the main surface after the precision polishing step.

(Construction 9)

The method of producing a glass substrate for a mask blank described in Construction 8, wherein the main surface of the glass substrate after the cleaning step has roughness of 0.2 nm or less in terms of the root mean square

roughness (RMS).

(Construction 10)

The method of producing a glass substrate for a mask blank described in Construction 7, wherein the step for eliciting a defect is carried out by etching the main surface.

(Construction 11)

The method of producing a glass substrate for a mask blank described in Construction 8 or 9, further having a defect inspection step that follows the cleaning step.

(Construction 12)

A method of producing a glass substrate for a mask blank whereby to produce a glass substrate by carrying out a rough polishing step for polishing a surface of the glass substrate by using abrasive particles having a predetermined average particle size, then a precision polishing step for polishing the surface of the glass substrate by using abrasive particles having an average particle size that is smaller than the aforesaid predetermined average particle size,

wherein, prior to the precision polishing step, the surface of the glass substrate is etched to elicit a crack, which extends from the surface of the glass substrate in the direction of the depth and remains after the precision polishing step, in a defect inspection step carried out after the precision polishing step.

(Construction 13)

The method of producing a glass substrate for a mask blank described in Construction 12, wherein a cleaning step for cleaning the main surface of the glass substrate is carried out after the precision polishing step.

(Construction 14)

The method of producing a glass substrate for a mask blank described in Construction 13, wherein the main surface of the glass substrate after the

cleaning step has roughness of 0.2 nm or less in terms of the root mean square roughness (RMS).

(Construction 15)

The method of producing a glass substrate for a mask blank described in Construction 13 or 14, wherein the cleaning step uses a solution having an etching function as a cleaning solution, and the cleaning step is carried out under a condition that causes the glass substrate to be removed by more than 0 μm and below 0.01 μm by etching.

(Construction 16)

The method of producing a glass substrate for a mask blank described in Construction 11 or 12, wherein the defect inspection step is implemented by a visual inspection.

(Construction 17)

The method of producing a glass substrate for a mask blank described in Construction 10 or 12, wherein the etching removes the surface of the glass substrate that is subjected to precision polishing by 0.01 to 0.2 μm.

(Construction 18)

The method of producing a mask blank, whereby a thin film that causes an optical change in response to transfer exposure light is formed on a main surface of the glass substrate obtained by the method of producing a glass substrate for a mask blank described in any one of Constructions 7 to 17.

(Construction 19)

A method of producing a transfer mask, wherein the thin film in the mask blank described in Construction 18 is patterned to form a thin film pattern.

According to the present invention, eliciting latent defects in the vicinity of a surface of the glass substrate for a mask blank permits easier detection of defects and provides the following specific industrially useful marked advantages.

1) It is possible to provide a glass substrate for an electronic device that has high smoothness that can be used for short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an EUV, etc., and a method of producing the same.

2) In addition to the above, it is possible to provide a glass substrate for a mask blank that has no surface defects on the major surface of the glass substrate and a glass substrate for a mask blank free of influences of a turned-down edge of an edge surface of the glass substrate, and a method of producing the same.

3) It is possible to provide a mask blank that has no under-film defects and can be securely loaded on a stepper of an exposure machine, and a method of producing the same.

4) It is possible to provide a transfer mask that has no pattern defects (pattern disconnection, etc.) and can be securely loaded on a stepper of an exposure machine, and a method of producing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flowchart illustrating a method of producing a glass substrate for an electronic device in accordance with the present invention;

Fig. 2 is a diagram showing the method of producing a glass substrate for an electronic device in accordance with the present invention;

Fig. 3 is a diagram showing the method of producing a glass substrate for an electronic device in accordance with the present invention;

Fig. 4 is a sectional view of the vicinity of a surface of a glass substrate before the step for eliciting latent defects;

Fig. 5 is a sectional view of the vicinity of the surface of the glass substrate after the step for eliciting latent defects; and

Fig. 6 is a flowchart illustrating a conventional method of producing a glass substrate for an electronic device.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Each of the constructions described above will be explained in conjunction with embodiments according to the present invention.

The glass substrate for a mask blank in Construction 1 is the glass substrate for a mask blank obtained by being subjected to post-processing steps, including a precision polishing step, after etching, and is characterized in that the surface roughness of the major surface of the glass substrate is 0.2 nm or less in terms of the root mean square roughness (RMS). Preferably, the surface roughness is 0.15 nm or less in terms of the root mean square roughness (RMS).

The surface roughness of the main surface of the glass substrate for a mask blank has high smoothness, specifically 0.2 nm or less in terms of the root mean square (RMS), making it possible to provide glass substrates for mask blanks that can be used for short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an EUV, etc.

In the glass substrate for a mask blank in Construction 2, the etching in Construction 1 is characterized by its operation for eliciting defects remaining on the major surface of the glass substrate. The etching that has the operation for eliciting defects remaining on the main surface of the glass substrate is carried out before a precision polishing step, thus making it possible to obtain a glass substrate for a mask blank that has high smoothness.
The defects remaining on the main surface of the glass substrate in this embodiment refer to concave surface defects, such as cracks.

The glass substrate for a mask blank in Construction 3 is characterized in that the surface defects of the main surface of the glass substrate in Construction 1 or 2 cannot be detected by visual inspection.

Since it is a glass substrate for a mask blank, the surface defects of the main surface of the glass substrate cannot be detected by a visual inspection

performed after precision polishing, which follows etching. Hence, a glass substrate with extremely high reliability can be provided, being free of surface defects that turn into under-film defects when the glass substrate is processed into a mask blank.

The glass substrate for a mask blank in Construction 4 is characterized in that the turned-down edge amount of the peripheral portion of the main surface of the glass substrate in any one of Constructions 1 to 3 is -2 μm to 0 μm. Restricting the turned-down edge amount of the peripheral portion to -2 μm to 0 μm permits improved positioning accuracy for loading the substrate on a stepper of an exposure machine.

The turned-down edge amount of the peripheral portion (end surface) of the main surface of the glass substrate is preferably -1 μm to 0 μm, and more preferably -0.5 μm to 0 μm. The turned-down edge amount is defined by the maximum height in the distance range of 3 mm from the boundary between the main surface and the chamfered surface when a virtual reference surface that extends 3 to 16 mm toward the center from the boundary between the main surface and the chamfered surface of the glass substrate is provided, and the height of the virtual reference surface is defined as 0, as shown in Fig. 2. Here, a negative (-) maximum height means that the peripheral portion of the main surface of the substrate has a turned-down configuration (a turned-down edge configuration), while a positive (+) maximum height means that the peripheral portion of the main surface of the substrate has a protuberant configuration.

The mask blank in Construction 5 is characterized in that a thin film that causes an optical change in response to transfer exposure light is formed on the main surface of the glass substrate for a mask blank in any one of Constructions 1 to 4. The mask blank uses the glass substrate for a mask blank in any one of Constructions 1 to 4, allowing the mask blank to be used for the short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an

EUV, etc. Thus, a mask blank can be obtained, which is free of under-film defects and can be securely loaded on a stepper of an exposure machine when the mask blank is processed into a transfer mask.

The transfer mask in Construction 6 is characterized in that a thin film pattern that causes an optical change in response to transfer exposure light is formed on the main surface of the glass substrate for a mask blank in any one of Constructions 1 to 4. The transfer mask uses the glass substrate for a mask blank in any one of Constructions 1 to 4, allowing the transfer mask to be used for the short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an EUV, etc. Thus, a transfer mask can be obtained, which is free of pattern defects (pattern disconnection or the like) and has a controlled turned-down edge on the glass substrate edge surface (the peripheral portion of the glass substrate main surface), so that the transfer mask can be securely loaded on a stepper of an exposure machine.

The method of producing a glass substrate for a mask blank in Construction 7 is a method of producing a glass substrate for a mask blank that has a step for eliciting a defect remaining on the main surface of the glass substrate, and is characterized in that a post-processing step that includes precision polishing is carried out after the step for eliciting a defect.

Since the step for eliciting a defect remaining on the main surface of a glass substrate is carried out before the post-processing step that includes precision polishing, a glass substrate for a mask blank that exhibits high smoothness can be obtained.

The defects remaining on the main surface of the glass substrate in this embodiment refer to concave surface defects, such as cracks.

The method of producing a glass substrate for a mask blank in Construction 8 is characterized in that the post-processing step in Construction 7 includes a precision polishing step for providing the main surface with

precision polishing and a cleaning step for cleaning the main surface after the precision polishing step.

Since the cleaning step for cleaning the main surface is carried out after the precision polishing step, the abrasive particles used in the precision polishing step or the foreign matters on the substrate surface can be removed. This makes it possible to obtain a glass substrate for a mask blank that is free of surface defects attributable primarily to substances stuck on the main surface of the glass substrate.

The cleaning solution used in the cleaning step may be an acid solution, such as a hydrofluoric acid, hydrofluorosilic acid or sulfuric acid solution, or an alkaline aqueous solution, such as a sodium hydroxide or potassium hydroxide, or pure water. To remove substances stuck on the main surface of the glass substrate, a solution having the etching function (an acidic solution or an alkaline aqueous solution) is preferred from the viewpoint of removing performance. The cleaning conditions, including the type and concentration of a chemical solution and time and temperature, are to be appropriately adjusted to set a predetermined amount of removal from the glass substrate by etching. The cleaning conditions are to be set such that the removal amount is more than 0 μm and below 0.01 μm in order to restrain the surface from being roughened by cleaning. From the viewpoint of cleaning performance, the use of hydrofluoric acid or hydrofluorosilic acid is desirable, and the concentration of the hydrofluoric acid or hydrofluorosilic acid is preferably low, 0.5% or less.

The method of producing a glass substrate for a mask blank in Construction 9 is characterized in that the main surface of the glass substrate after the cleaning step in Construction 8 has roughness of 0.2 nm or less in terms of the root mean square roughness (RMS).

The main surface of the glass substrate has high smoothness, the surface roughness being 0.2 nm or less in terms of root mean square

roughness (RMS), thus making it possible to provide a glass substrate for a mask blank for the short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an EUV, etc. Preferably, the surface roughness is 0.15 nm or less in terms of the root mean square roughness (RMS).

The method of producing a glass substrate for a mask blank in Construction 10 is characterized in that the step for eliciting a defect in Construction 9 is carried out by etching the main surface of the glass substrate. The production method allows a defect remaining on the main surface to be effectively elicited and provides cleaning effect, thus making the production method desirable.

The method of producing a glass substrate for a mask blank in Construction 11 is characterized by further including a defect inspection step that follows the cleaning step in Construction 8 or 9. After the cleaning step, the defect inspection step is carried out so as to select glass substrates free of surface defects, thus making it possible to provide glass substrates with extremely high reliability, having no surface defects that lead to pattern defects.

The method of producing a glass substrate for a mask blank in Construction 12 is a method of producing a glass substrate for a mask blank whereby to make a glass substrate by carrying out a rough polishing step for polishing a surface of the glass substrate by using abrasive particles having a predetermined average particle size, then a precision polishing step for polishing the surface of the glass substrate by using abrasive particles having an average particle size that is smaller than the aforesaid predetermined average particle size. The production method is characterized in that, prior to the precision polishing step, the surface of the glass substrate is etched to elicit a crack, which extends from the surface of the glass substrate in the direction of the depth and remains after the precision polishing step, in a defect inspection step carried out after the precision polishing step.

A glass substrate for a mask blank can be obtained that has no surface defects on the main surface of the glass substrate and a less turned-down edge on a glass substrate edge surface (the peripheral portion of the main surface of the glass substrate).

The rough polishing step in the present invention is carried out to remove scratches from the main surface of a glass substrate formed by a grinding step or the like so as to maintain the flatness obtained by the grinding step. In the rough polishing step, relatively large abrasive particles having the average particle size of about 1 μm to about 3 μm are used.

The material of the abrasive particles is appropriately selected mainly according to the material of the glass substrates. For example, a cerium oxide, a zirconium oxide or the like is used.

The rough polishing step may include a single cycle or a plurality of cycles. The polishing pad used in the rough polishing step may be either a hard polisher or a soft polisher.

The precision polishing step in the present invention is carried out to remove, by the rough polishing step or the like described above, the texture formed on the main surface of the substrate so as to provide the substrate with a mirror finished surface. The step uses relatively small abrasive particles having an average particle size of about 1 μm or less (e.g., 30 nm to 1 μm). The material of the abrasive particles is appropriately selected according mainly to the material of the glass substrate, as in the case set forth above. Preferably, colloidal silica is used, because it has a small average particle size and permits a smooth substrate surface to be obtained. Moreover, using the colloidal silica for the abrasive particles makes it possible to provide the main surface of the glass substrate with a mirror finish by precision polishing, so that the cracks remaining after the precision polishing step exist in the smooth surface state, allowing the cracks to be easily detected. From the viewpoint of the mirror

finish, the average particle size is preferably small. Furthermore, the polishing pad used in the precision polishing step is preferably a soft or supersoft polisher to achieve the mirror finish. The surface roughness of the mask blank glass substrate that is lastly obtained after the precision polishing step is preferably 0.2 nm or less in terms of an average surface roughness, namely, a center-line mean roughness Ra and further 0.2 nm or less in terms of the root mean square roughness (RMS).

To elicit cracks in the defect inspection step carried out after the precision polishing step in the present invention means to enlarge, by etching, the latent cracks that cannot be or are difficult to be visually checked before etching and to make it possible to check them more clearly by precision polishing. For example, etching enlarges such latent cracks to such sizes that make the cracks in a glass substrate recognizable in the defect inspection step carried out after the precision polishing step. Specifically, the cracks are enlarged to a width that allows the defects to be recognized in the visual inspection in Construction 15. The cracks are preferably enlarged to a width of 0.2 μm or more on the glass substrate surface.

The etching described in Constructions 1, 2, 10 and 12 set forth above is performed before the precision polishing step aimed at providing the glass substrate surface with a mirror finish. The etching may be performed before the rough polishing step, or after the rough polishing step and before the precision polishing step, or both before the rough polishing step and before the precision polishing step following the rough polishing step. To remove surface defects after the precision polishing step, the etching is preferably carried out at least after the rough polishing step and prior to the precision polishing step.

For the etching, either the dry etching method or the wet etching method may be used.

The cracks are magnified by the etching. For instance, if the wet etching is performed, a crack extending from the glass substrate surface toward the center is isotropically etched. Hence, the depth of the crack toward the center does not change much due to the amount of etching on the glass substrate surface, whereas the size (width) of the crack in the direction of the surface increases. In the present invention, the etching step is carried out before the precision polishing step, then the precision polishing for mirror finishing is implemented. Hence, in the defect inspection step carried out after the precision polishing step, the glass substrate surface, which has been turned into an extremely smooth surface by the precision polishing step, makes it easy to detect the crack having the certain size (width) by the etching, the crack being present in the smooth surface.

Furthermore, since the etching is performed before the precision polishing (especially when the etching is performed after the rough polishing step but before the precision polishing step), the glass substrate surface becomes relatively even. This makes it possible to restrain the load in the precision polishing step for turning the glass substrate surface to a mirror surface, and to improve the configuration of an edge surface of the glass substrate (to reduce the amount of the turned-down edge of the peripheral portion of the main surface of the glass substrate).

In the precision polishing step, glass substrates are generally polished using polishing pads of soft polishers or supersoft polishers, so that the edge surfaces of glass substrates tend to develop turned-down edges as the polishing time passes. As discussed above, however, the load in the precision polishing step can be restrained, thus permitting the amount of the turned-down edge of a glass substrate edge surface to be controlled.

The amount of the turned-down edges of the glass substrate edge surfaces (the peripheral portions of the main surfaces of the glass substrate)

can be controlled to -2 μm to 0 μm, and may be preferably controlled to -1 μm to 0 μm, and further preferably to -0.5 μm to 0 μm.

The cracks refer to fissures that extend in the direction of depth from the surfaces of glass substrate. The cracks are produced in a grinding step or a polishing step before a finish polishing step that uses abrasive particles having a relatively large particle size (e.g., a polishing step using cerium oxide as a primary abrasive), and hardly have widths on the surfaces of glass substrate, making it almost impossible to detect them. The problematic cracks in the present invention refer to the cracks remaining after the precision polishing step, that is, the cracks having such depths that cannot be removed by the precision polishing step. In other words, if the cracks are shallow enough to be removed by the precision polishing step, then they will disappear after the precision polishing step.

The etching is preferably performed using an alkaline aqueous solution. Here, the alkaline aqueous solution is preferably an aqueous solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) or the like or a mixed solution of these.

The method of producing a glass substrate for a mask blank in Construction 13 is characterized in that a cleaning step for cleaning the main surface of a glass substrate is carried out after the precision polishing step in Construction 12.

The cleaning step for cleaning the main surface is carried out after the precision polishing step, so that the abrasive particles used in the precision polishing step or the foreign matters or the like stuck to the substrate surface can be removed, thus making it possible to obtain a glass substrate for a mask blank free of surface defects attributable mainly to the substances stuck to the main surface of the glass substrate.

The method of producing a glass substrate for a mask blank in Construction 14 is characterized in that the main surface of a glass substrate after the cleaning step in Construction 13 has roughness of 0.2 nm or less in terms of the root mean square roughness (RMS).

The surface roughness of the main surface of the glass substrate has high smoothness, specifically 0.2 nm or less in terms of the root mean square roughness (RMS), making it possible to provide glass substrates for mask blanks that can be used for short wavelength ranges of an ArF excimer laser, an F2 excimer laser, an EUV, etc. Preferably, the surface roughness is 0.15 nm or less in terms of the root mean square roughness (RMS).

The method of producing a glass substrate for a mask blank in Construction 15 is characterized in that the cleaning step uses a solution having an etching function as a cleaning solution, and the cleaning step is carried out under a condition that causes the glass substrate to be removed by more than 0 μm and below 0.01 μm by etching in Construction 13 or 14.

Normally, the cleaning carried out mainly to remove abrasive particles or foreign matters stuck to a substrate surface uses a detergent, acid, alkali or the like. When a cleaning solution (acid, alkali) having an etching function for glass substrates is used, the cleaning step is carried out under a condition such that the surface of the glass substrate is removed by more than 0 μm and below 0.01 μm. This is because, if the amount of removal by etching in the cleaning step is 0.01 μm or more, then etching residues causes unevenness.

The method of producing a glass substrate for a mask blank in Construction 16 is characterized in that a defect inspection step is implemented by a visual inspection in Construction 11 or 12.

There are no particular restrictions on the defect inspection method. The defect inspection may be performed by visual inspection or by using a defect inspection apparatus that carries out the defect inspection by applying

inspection light to glass substrates and detect scattered light or the light leaked out of the glass substrates. However, visual inspection is preferred because it is advantageous in efficiency and certainty of inspection and in determining the types of defects.

The method of producing a glass substrate for a mask blank described in Construction 17 is characterized in that the etching removes the surface of the glass substrate that is subjected to precision polishing by 0.01 to 0.2 μm in Construction 10 or 12.

An amount of etching below 0.01 μm is not desirable, because it would make it difficult to determine the presence of a crack in the defect inspection step carried out after the precision polishing step. On the other hand, an amount of etching over 0.2 μm is not desirable, either, because the surface roughness and the surface configuration (flatness) would deteriorate as a result of the etching of the glass substrate.

The etching rate in the etching process is preferably 0.2 nm/min. to 2.0 nm/min. An etching rate below 0.2 nm/min. is not desirable, because it would not sufficiently elicit latent defects. On the other hand, an etching rate over 2 nm/min. is not desirable, either, because it would badly affect the surface roughness and the surface configuration (flatness) due to quick corrosion of the glass substrate. A preferable range is 0.3 nm/min. to 0.7 nm/min.

The method of producing a glass substrate for a mask blank in Configuration 18 is characterized in that a thin film that causes an optical change in response to transfer exposure light is formed on the main surface of the glass substrate obtained by the method of producing a glass substrate for a mask blank described in any one of Constructions 7 to 17. The glass substrates free of surface defects that have been obtained by removing the glass substrates with cracks remaining therein that have been obtained in Constructions in 7 to 17,. so that mask blanks free of under-film defects can be

obtained.

The method of producing a transfer mask in Construction 19 is characterized in that the thin film of the mask blank in Construction 18 is patterned to form a thin film pattern. The transfer mask is fabricated by using a mask blank free of under-film defects that has been obtained in Construction 17, making it possible to obtain a transfer mask that is free of pattern defects (pattern disconnections) and can be securely loaded on a stepper of an exposure machine.

The mask blank in the present invention is used as a generic term, and includes a photomask blank in which only a light shielding film that has a function for blocking transfer exposure light is formed on the main surface of a glass substrate, a phase shift mask blank having a phase shift film that has a phase shift function for causing a phase difference change in response to transfer exposure light, and a reflective mask blank having a reflective film that reflects transfer exposure light or an absorbent film that absorbs transfer exposure light.

The mask blanks further include other types of mask blanks, including the ones with resist films deposited on the foregoing light shielding film, phase shift film, reflective film, or the like.

There are no particular restrictions on the material of the glass substrate in the present invention. Materials used for the glass substrate in the present invention include silica glass, non-alkali glass, soda lime glass, and alumino borocilicic acid glass. Silica glass, in particular, is a hard, brittle material, as compared with other glass materials, so that the surface of a glass substrate easily develops cracks in a grinding step or a rough polishing step. For this reason, the glass substrate for a mask blank and the method of producing the same described above are especially effective when the material of the glass substrate is silica glass.

Embodiment 1

The following will explain a method of producing a glass substrate for a mask blank in accordance with the present invention. In the following explanation, the glass substrate for a mask blank is referred to as the glass substrate for an electronic device.

The method of producing a glass substrate for an electronic device in accordance with the present invention will be explained with reference to Fig. 1.

The method of producing a glass substrate for an electronic device shown in Fig. 1 includes:

a rough polishing step for polishing, with relatively large abrasive particles, both main surfaces of a glass substrate for an electronic device that has been subjected to the shaping of the glass substrate and the grinding of the both main surfaces of the substrate by a lapping machine or the like (S101);

an etching step for eliciting a latent crack that extends in the direction of the depth from a surface of a glass substrate by etching (S102);

a precision polishing step for polishing with relatively small abrasive particles (S103); and

a defect inspection step (S104) for inspecting defects in the glass substrate.

The defect inspection step (S104) in Fig. 1 is carried out in order to exclude, as defectives, the glass substrates with still remaining defects after the precision polishing step is carried out to provide the main surfaces of the glass substrates with mirror finish.

The processing conditions of the aforesaid etching step (S102) is determined as set forth below.

In the aforesaid defect inspection step (S104), conditions are to be set such that cracks extending in the depth direction from the surfaces of glass substrates are magnified to sizes that permit the cracks to be securely detected

and checked and to be elicited. The cracks remaining after the precision polishing step are magnified by etching performed before the precision polishing step. The etching conditions are set so as to allow such cracks to be detected and checked accurately and securely in the defect inspection step following the precision polishing step. More specifically, the etching conditions are set such that the amount of removal by etching is 0.01 to 0.2 μm. This makes it possible to enlarge cracks to widths of 0.2 μm or more on the surfaces of glass substrates, so that the defects existing on the surface of the glass substrates can be securely detected and checked.

Further preferably, after the step (S102) is carried out such that the flatness of glass substrates and the turned-down edge amount of the edge surfaces of the glass substrates will be within a predetermined range (specifically, the flatness and the turned-edge amount that allow a predetermined pattern position accuracy to be obtained when transfer masks (e.g., photomasks) are made using glass substrates and the photomasks are loaded on the steppers of an exposure machine) after the precision polishing step aimed at providing glass substrates with mirror finish. This causes the surfaces of the glass substrates to be relatively smooth, and the polishing-off amount in the precision polishing step can be reduced (the load in the precision polishing step for mirror finish is reduced). Preferably, therefore, the conditions are set so as to permit reduced variation in the substrate edge surfaces in the precision polishing step.

Preferably, therefore, the etching speed in the etching process is relatively slow. Specifically, the etching speed is set to 0.2 nm/min. to 2 nm/min. It is desirable to use an alkaline aqueous solution having a mild etching action on glass substrates.

In the production method shown in Fig. 1 discussed above, the polishing method in the rough polishing step and the precision polishing step may be a

single-sided polishing method or a both-sided polishing method. Further, a sheet system or a batch system may be used.

Furthermore, in the production method shown in Fig. 1, a cleaning step is provided, as necessary, to remove abrasive particles so as to prevent the abrasive particles used in the rough polishing step or the precision polishing step from being carried over to the next step, and also to remove foreign matters stuck to the surfaces of glass substrates. As for the cleaning methods, one or multiple cleaning methods are selected according to the objects to be removed, the cleaning methods including the cleaning methods using chemical solutions (acid or alkali), detergents, pure water or ultrapure water, a wet cleaning method using a functional water, such as hydrogen water, and dry cleaning methods involving the application of UV (ultra-violet rays) or ozone treatment.

When the cleaning is performed using a chemical solution that effects an etching action on glass substrates, the etching removal amount is preferably set to be over 0 μm and below 0.01 μm, and preferably over 0 μm and below 0.005 μm so as not to cause irregularities to be formed due to etching residues.

Fig. 3 through Fig. 5 are sectional views of the vicinity of a surface of a glass substrate before and after cracks are elicited by etching performed with an alkaline aqueous solution. For easier understanding of the explanation, the amount to be polished off in the precision polishing step is set to 1 μm in the explanation.

Fig. 3 is a sectional view of the vicinity of the surface of the glass substrate before etching, the glass substrate having undergone the rough polishing step.

The surface of a glass substrate 1 after the rough polishing step has not been fully turned into a mirror surface, and the entire surface of the substrate has irregularities like textures. A fissure-like crack 2 formed from the surface of

the glass substrate 1 toward the center exists at places where the texture-like irregularities are formed. The cracks are formed in a grinding step or a rough polishing step using abrasive particles of relatively large particle sizes. Various cracks exist, including cracks 21 and 22 having depths that exceed 1 μm, and a crack 23 having a depth below 1 μm.

The shallow crack 23 is removed by the subsequent precision polishing step, whereas the cracks 21 and 22 having depths of 1 μm or more that is greater than the polishing-off amount in the precision polishing step cannot be removed by the subsequent precision polishing step.

In the state illustrated in Fig. 3, the cracks existing on the surface of the glass substrate cannot be visually checked.

Fig. 4 is a sectional view showing the vicinity of the surface of the glass substrate after etching.

In Fig. 4, the dotted lines indicate the surface of the glass substrate before etching, while the solid line indicates the substrate surface after etching.

The surface of the glass substrate is isotropically etched in the direction of the inside the surface and the depth by etching, so that the crack 2 is magnified. In this state, however, the glass substrate surface hardly shows a difference from the state illustrated in Fig. 3. Hence, even if the crack has been enlarged, the crack is hidden behind the texture irregularities, making it difficult to be visually checked, and overlooked in some cases.

Fig. 5 is a sectional view of the vicinity of a surface of a glass substrate that has undergone the precision polishing step.

The surface of the glass substrate 1 after the precision polishing step has a mirror finish with average surface roughness Ra of 0.2 nm or less.

As shown in Fig. 5, the cracks present at the positions deeper than a polishing-off amount in the precision polishing step, the depths thereof from the surface of the glass substrate being over 1 μm are enlarged by etching, as

illustrated. Since the enlarged cracks 31 and 32 are present in the mirror surface state of the surface of the glass substrate 1, they can be detected securely and easily in the defect inspection step (visual inspection) after the precision polishing step.

<First embodiment> (Method of producing the glass substrate for an electronic device shown in Fig.1)

(1) Rough polishing step

Twelve synthetic silica glass substrates (6 inch x 6 inch (1 inch = 25.4 mm)) having edge surfaces thereof shaped and having been ground by a double-side lapping apparatus were loaded on a batch type double-side polishing apparatus, and subjected to rough polishing under the following polishing conditions. The machining load and the polishing conditions were adjusted, as necessary.

Polishing solution: Cerium oxide (average particle size: 1 to 2 μm) + water

Polishing pad: Hard polisher (urethane pad)

After the rough polishing, the glass substrates were cleaned by immersing them in an aqueous solution containing hydrofluorosilic acid to remove the polishing abrasive particles from the glass substrates.

The measurements of the surface roughnesses of the main surfaces of the obtained glass substrates by using an atomic force microscope (AFM) indicated an average surface roughness Ra of 0.25 nm.

(2) Etching step

Then, the obtained glass substrates were immersed in a chemical solution (alkali: sodium hydroxide) to remove the surfaces of the glass substrates by about 0.05 nm by etching so as to magnify the cracks existing in the vicinities of the surfaces of the glass substrates. The concentration of the chemical solution used for this purpose was set so that the etching rate with

respect to the glass substrates was 0.8 nm/min. The measurements of the surface roughnesses of the main surfaces of the obtained glass substrates by using the atomic force microscope indicated the average surface roughness Ra of 0.23 nm, verifying that the surface configurations are slightly smoother.

(3) Precision polishing step

The twelve obtained glass substrates were loaded on the aforesaid double-side polishing apparatus, and subjected to precision polishing under the following polishing conditions. The machining load and the polishing conditions were adjusted, as necessary. (The polishing time was set so as to minimize a configuration change of substrate end surfaces caused by the precision polishing and to be long enough to turn the surfaces of the glass substrates into mirror surfaces (a polishing time was set so as to polish off about 1 μm)).

Polishing solution: Colloidal silica (average particle size: 50 to 80 nm) + water

Polishing pad: Soft polisher (suede type)

After the precision polishing, the glass substrates were cleaned by immersing them in a cleaning tank of an alkaline aqueous solution to remove the polishing abrasive particles from the glass substrates. The conditions of cleaning by using the alkaline aqueous solution were set such that the amount of removal by etching the glass substrates was about 0.005 μm.

The measurements of the surface roughnesses of the main surfaces of the obtained glass substrates by using an atomic force microscope (AFM) indicated that the average surface roughness Ra was 0.14 nm, or 0.18 nm in terms of the root mean square roughness RMS. Thus, the main surfaces of the glass substrates obtained the high smoothness with successful mirror finish.

(4) Defect inspection step

When the twelve obtained glass substrates were visually inspected for defects, a surface defect presumably due to a magnified crack was recognized

in one out of the twelve glass substrates. No surface defects, such as cracks, were recognized in the remaining ten glass substrates.

The measurement of the configurations of the glass substrate edge surfaces (turned-down edge amounts) performed by a stylus type roughness gauge (Surftest 501) according to the above definition indicated good results, the turned-down edge amounts of all the glass substrates lying within the range of -0.5 μm to -0.25 μm. Furthermore, the measurement of the flatness of the main surfaces of the glass substrates performed using a flatness measuring instrument (FM200 made by Troppel) indicated good results, the flatness of all the main surfaces of the glass substrates being 1 μm or less.

The obtained glass substrates can be used as the glass substrates for the mask blanks for ArF excimer lasers and the glass substrates for the mask blanks for F2 excimer lasers.

Second Embodiment

Glass substrates were fabricated in the same manner as that in the first embodiment except for some changes in the cleaning step after the completion of the precision polishing step in the first embodiment. Specifically, the immersion time of the cleaning conditions, in which the glass substrates are cleaned by immersing them in a cleaning tank of a low-concentration of hydrofluorosilic acid (concentration: 0.15%) to remove the polishing abrasive particles from the glass substrates, was set such that the amount of removal by etching on the glass substrates would be about 0.003 μm.

The measurements of the surface roughnesses of the main surfaces of the obtained glass substrates by using an atomic force microscope (AFM) indicated an average surface roughness Ra of 0.09 nm, or 0.15 nm in terms of the root mean square roughness RMS. Thus, the main surfaces of the glass substrates obtained the high smoothness with successful mirror finish.

When the twelve obtained glass substrates were visually inspected for

defects, a surface defect presumably due to a magnified crack was recognized in one out of the twelve glass substrates. No surface defects, such as cracks, were recognized in the remaining eleven glass substrates.

The measurement of the configurations of the glass substrate edge surfaces (turned-down edge amounts) performed by a stylus type roughness gauge (Surftest 501) according to the above definition indicated good results, the turned-down edge amounts of all the glass substrates lying within the range of -0.5 μm to -0.25 μm. Furthermore, the measurement of the flatness of the main surfaces of the glass substrates performed using the flatness measuring instrument (FM200 made by Troppel) indicated good results, the flatness of all the main surfaces of the glass substrates being 1 μm or less.

The obtained glass substrates can be used as the glass substrates for the mask blanks for EUV.

<First and Second Comparative Examples>

Glass substrates for electronic devices were fabricated under the same conditions according to the method of producing the glass substrate for an electronic device in the first embodiment except that the etching process in (2) was not carried out (first comparative example).

Glass substrates for electronic devices were fabricated under the same conditions according to the method of producing the glass substrate for an electronic device in the first embodiment except that the etching process in (2) was not carried out, and the polishing conditions in the precision polishing step of (3) were changed. Specifically, the polishing time required to obtain the polishing-off amount to completely remove scratches in the rough polishing step in (1) (the polishing time for obtaining a polishing-off amount of 5 μm) was set (second comparative example).

When the glass substrates for electronic devices in the second comparative example were visually checked for defects, all glass substrates

indicated satisfactory polishing-off amounts, whereas the configurations of glass substrate edge surfaces (turned-down edge amounts) of all the glass substrates indicated deterioration, the turned-down edge amounts being all below -2.0 μm. The results of measurement of the flatness of the main surfaces of the glass substrates performed using a flatness measuring instrument (FM200 made by Troppel) indicated deteriorated flatness, the flatness of all the main surfaces of the glass substrates being over 1 μm (some being over 2 μm).

The glass substrates for electronic devices in the first comparative example were visually inspected for defects, but no surface defects were recognized.

<Evaluation after fabricated into photomask blanks and photomasks>

Photomask blanks were fabricated by depositing a chromium nitride film, a chromium carbide film and a chromium oxynitride film (total film thickness: 900 angstroms) by sputtering on one main surface of each of the glass substrates obtained in the first embodiment and the first and second comparative examples described above. In addition, a phase shift mask blank was fabricated by forming a nitrified molybdenum silicide film (film thickness: 800 angstroms) by sputtering on one main surface of each of the glass substrates obtained in the first embodiment and the first and second comparative examples described above. After depositing the film, scrub cleaning was performed to fabricate photomask blanks and phase shift mask blanks.

The obtained photomask blanks and the phase shift mask blanks were inspected using a surface defect inspection apparatus. No under-film defects were found in the first embodiment (the glass substrates for electronic devices free of concave surface defects) and the photomask blanks fabricated using the glass substrates for electronic devices in the second comparative example. However, under-film defects were found in three out of twelve photomask

blanks fabricated using the glass substrates for electronic devices in the first comparative example (when the films formed on the glass substrates were peeled off and the surfaces of the glass substrates were process by the etching in (2), the configurations of the defects were found to be similar to that of the concave surface defect found in one of the twelve glass substrates in the defect inspection step in the first embodiment. The defects are considered to be the cracks magnified by etching.)

Here, the foregoing results will be reviewed. According to the method of producing the glass substrates for electronic devices in the first embodiment, the cracks on the glass substrates are magnified by performing the alkali treatment before the precision polishing step to allow surface defects to be found in the defect inspection step after the precision polishing step, thus making it possible to produce photomask blanks by using glass substrates free of surface defects. This enables photomask blanks free of under-film defects to be obtained. However, according to the method of producing the glass substrates for electronic devices in the first comparative example, the glass substrates are fabricated without magnifying cracks existing in the glass substrates and subjected to the defect inspection. Therefore, the glass substrates having surface defects, which should be have been checked, are determined to be non-defective, and sent to the production process of the photomask blanks. As a result, photomask blanks with under-film defects were obtained, causing the production yield of the photomask blanks to be significantly reduced.

Furthermore, resist films were deposited on the aforesaid films by spin coating to make photomasks and phase shift masks having desired patterns.

As a result, no pattern defects, such as pattern disconnection, were found in the photomasks composed of the photomask blanks free of under-film defects and the photomask blanks in the second comparative example among

the photomask blanks fabricated by using the glass substrates for electronic devices in which no concave surface defects have been found in the first embodiment, and the photomask blanks fabricated using the glass substrates for electronic devices in the first comparative example.

However, pattern defects, such as pattern disconnection, were found when photomasks were made by using the photomask blanks, in which under-film defects had been found, among the photomask blanks made by using the glass substrates for electronic devices in the first comparative example.

Next, in order to conduct a substrate deformation test, a board holding testing machine adapted to vacuum-chuck two sides of a substrate was prepared to simulate the loading onto the steppers of an exposure machine. The flatness changes observed when loading the obtained photomasks discussed above were measured by an optical interferometer (Zygo Mark GPI). The flatness changes of the photomasks fabricated by using the glass substrates for electronic devices in the first embodiment and the first comparative example were 0.1 μm, showing very little changes. The flatness changes of the photomasks fabricated by using the glass substrates for electronic devices in the second comparative example exceeded 0.5 μm, and loading failure attributable to turned-down edges was found.

The description has been given of the preferred embodiments of the production method in accordance with the present invention. The present invention is, however, not limited to the contents described in conjunction with the above embodiments, and includes the contents described in conjunction with the means for solving the above problems.

The present invention makes it possible to obtain the glass substrates for electronic devices having high smoothness that can be used for the short wavelength ranges of ArF excimer lasers, F2 excimer lasers, EUVs, etc. Furthermore, the description has been given of the glass substrates for mask

blanks as most useful examples in the embodiment set forth above; however, the production method in accordance with the present invention can be also applied to the glass substrates for liquid crystal displays, the glass substrates for information recording media (magnetic disks, magneto-optical disks and optical disks), and semiconductor wafers or the like. The configurations of the substrates are mainly square (e.g., rectangular (quadrate or rectangular)), discoid or substantially round. Rectangular substrates include the glass substrates for mask blanks, such as photomask blanks, phase shift blanks and reflective mask blanks, and the glass substrates for liquid crystal displays. Discoid substrates include the glass substrates for information recording media, and circular substrates include semiconductor wafers, etc.